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(21) International Application Number: PCT/US93/03119 (22) International Filing Date: 2 April 1993 (02.04.93) (30) Priority data: 07/862,683 3 April 1992 (03.04.92) US (71) Applicant: EXXON CHEMICAL PATENTS INC. [US/ US]; 5200 Bayway Drive, Baytown, TX 77520 (US). (72) Inventors: TERRY, Donna, Jeanes ; 7103 Winding Walk Drive, Houston, TX 77095 (US). GADKARI, Avinash. Chandrakant ; 696 Pineloch Drive, Apt. 1708, Webster, TX 77598 (US).		(74) Agents: BELL, Catherine, L. et al.; Exxon Chemical Com- pany, P.O. Box 2149, Baytown, TX 77522-2149 (US). (81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: POLYMERIC STABILIZERS FOR POLYOLEFINS (57) Abstract The present invention provides for polymeric stabilizers which are the acid-catalyzed reaction product of a phenolic compound or a ring substituted aromatic compound and an olefin polymer containing either terminal unsaturation and/or pendant unsaturation along the polymer chain. These stabilizers are readily compatible with olefin polymer and copolymer matrixes and offer good protection of the matrix polymer against one or more of heat, oxygen, ultra violet or radiation degradation. Other advantages include low volatilization as well as low tendency to migrate from the polymer matrix.		

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POLYMERIC STABILIZERS FOR POLYOLEFINS

BACKGROUND OF THE INVENTION

Field of the Invention

1
2 This invention relates to a novel class of polymeric stabilizers based on
3 the reaction product of an unsaturated olefin polymer and a substituted
4 aromatic or phenolic compound, and the use of these reaction products
5 as stabilizers for olefin polymers.
6

Description of Related Art

7
8
9 Certain phenolic compounds and derivatives thereof have been used to
10 stabilize olefin polymers against polymer breakdown caused by
11 processing these polymers at high temperatures. Examples of such
12 materials would include alkylated monophenols, alkylated
13 hydroquinones, alkyl substituted bis phenols and hindered phenolic
14 benzyl compounds.
15

16 Several problems are associated with the use of these materials. They
17 are generally not very compatible with olefin polymers due to their
18 aromatic structure and also due to the presence of one or more polar
19 (hydroxy) substituents in the aromatic nucleus. Thus it may be difficult
20 to uniformly disperse the phenolic stabilizer within the polymer matrix
21 or prevent it from migrating out of the polymer. Secondly, these
22 materials are quite volatile at temperatures at which the matrix polymer
23 is processed and/or extruded, and consequently a significant loss of
24 stabilizer may be realized during the polymer processing due to
25 evaporation.
26

1 It has been proposed in the prior art that the problem of volatility and,
2 to some degree, compatibility can be minimized by providing phenolic-
3 based stabilizers which are themselves polymeric. For example, British
4 patent specification 1483067 discloses polymeric stabilizers prepared by
5 reacting a phenolic compound with a liquid polymeric material such as
6 polypropylene or polybutene in the presence of a Friedel-Crafts type
7 catalyst to provide a phenol compound alkylated with the polymer
8 reactant. These polymer reaction products are said to have little
9 volatility at temperatures employed in polymer processing (200-280°C)
10 and to be more compatible with a polymer matrix because of suitable
11 matching of the polymer chain joined to the molecule of the phenol and
12 the matrix polymer.

13
14 Alkylated phenols similar to those described above are also disclosed in
15 British Patent Specification 1159368 wherein the polymeric alkylating
16 agent may also include low molecular weight liquid polypropylene as
17 well as higher molecular weight polyolefins such as polybutene and butyl
18 rubber.

19
20 The stabilizers referred to above suffer from the deficiency that they are
21 either very low molecular weight amorphous materials (polymer Mn
22 below about 500) or that the degree to which the phenolic compounds
23 are alkylated is difficult to control. Also, in the case of British
24 Specification 1,159,368, the positioning of the phenolic substituent
25 groups along higher molecular weight polymer chains can not be readily
26 tailored but is rather an arbitrary function of the reaction chemistry.
27 These variables can effect the compatibility of the polymeric stabilizers
28 with the matrix olefin-based polymers to which they are added to impart
29 stability, as well as the physical properties of the matrix polymers.

30 31 Summary of the Invention

32
33 The present invention provides for polymeric stabilizers which are the
34 acid-catalyzed reaction product of a phenolic compound or a ring
35 substituted aromatic compound and an olefin polymer containing either

1 terminal unsaturation and/or pendant unsaturation along the polymer
2 chain. These stabilizers are readily compatible with olefin polymer and
3 copolymer matrixes and offer good protection of the matrix polymer
4 against one or more of heat, oxygen, ultra violet or radiation
5 degradation. Other advantages include low volatilization as well as low
6 tendency to migrate from the polymer matrix.

7
8 Detailed Description of the Invention

9
10 Olefin polymers which are used to prepare the stabilizers of the present
11 invention may be characterized as amorphous or crystalline
12 homopolymers or copolymers of C_1 to C_{20} monoolefins

13
14 wherein the polymer chains contain residual double bonds either at
15 the terminal or pendant positions.

16
17
18 These double bond sites which may comprise ethenylidene (vinyl or
19 vinylidene) type unsaturation, serve as the reaction sites for facile
20 electrophilic aromatic substitution reactions with phenolic compounds
21 or ring substituted aromatic compounds as hereinafter described, to
22 produce polymer alkylated phenolics or aromatics useful as stabilizers
23 for olefin polymers.

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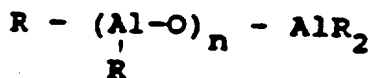
Preferred olefin polymers useful in preparing the stabilizers of this invention include homopolymers of C_2 to C_{20} monoolefins and copolymers thereof which contain unsaturation at the terminal position of the polymer chain. These polymers are also known in the art and are commonly produced with single site catalyst systems which typically comprise a metallocene (bridged or unbridged species wherein the cyclopentadienyl group(s) are substituted or unsubstituted and are the same or different; the bridging group may also be substituted or unsubstituted) and either an organoaluminum cocatalyst or an ionic activator component. The catalyst system may also be prepolymerized with the olefin monomer(s) if so desired. The catalyst employed may optionally be supported on an inert, organic or inorganic media. The catalysts chosen may be placed on a supported media by methods generally known to those skilled in the art.

The metallocenes which may be employed to prepare the catalysts comprise one or a mixture of organometallic coordination compounds which are cyclopentadienyl derivatives of Group 4b, 5b, or 6b metals of

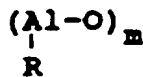
the Periodic Table. These metallocene compounds include mono, di and tricyclopentadienyls and their derivatives of the transition metals. Particularly preferred are the metallocenes of Group 4b or 5b metals such as titanium, zirconium, hafnium and vanadium.

Some preferred metallocenes are bis(cyclopentadienyl)zirconium; dimethyl bis(cyclopentadienyl) zirconium dichloride; bis(cyclopentadienyl) titanium dichloride; bis(methylcyclopentadienyl) zirconium dichloride; bis(methylcyclopentadienyl) titanium dichloride; bis(n-butylcyclopentadienyl)zirconium dichloride; dimethylsilyldicyclopentadienyl zirconium dichloride; bis(trimethylsilylcyclopentadienyl) zirconium dichloride; and dimethylsilyldicyclopentadienyl titanium dichloride; bis(indenyl) zirconium dichloride; bis (4,5,6,7-tetrahydro-indenyl)zirconium dichloride; the racemic and/or meso isomer of 1,2-ethylene-bridged bis(4,5,6,7-tetrahydroindenyl)zirconium dichloride; the racemic and/or meso isomer of 1,1-dimethyl-silyl-bridged bis(4,5,6,7-tetrahydroindenyl) zirconium dichloride; and the racemic and/or meso isomer of 1,1-dimethylsilyl-bridged bis(methyl-cyclopentadienyl) zirconium dichloride. Monocyclopentadienyl zirconium may also be employed.

The alumoxanes are known materials and comprise oligomeric, linear alumoxanes of the formula:



or oligomeric, cyclic alumoxanes of the formula:



wherein n is 1-40, m is 3-40, and R and R₂ are independently an alkyl group having from 1-5 carbon atoms.

1 The alumoxane can be prepared in various ways. Preferably, they are
2 prepared by contacting water with a solution of aluminum trialkyl, such
3 as, for example, aluminum trimethyl, or aluminum triethyl, in a suitable
4 organic solvent such as toluene or an aliphatic hydrocarbon. For
5 example, the aluminum alkyl may be treated with water in the form of a
6 moist solvent. In an alternative method, the aluminum alkyl such as
7 aluminum trimethyl can be desirably contacted with a hydrated salt such
8 as hydrated copper sulfate or ferrous sulfate. The water may be
9 contained in a carrier such as silica. Preferably, the
10 alumoxane is prepared in the presence of a hydrated ferrous sulfate.
11 The method comprises treating a dilute solution of aluminum trimethyl
12 in, for example, toluene, with ferrous sulfate represented by the general
13 formula $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. The ratio of ferrous sulfate to aluminum
14 trimethyl is desirably about 1 mole of ferrous sulfate for 6 to 7 moles of
15 aluminum trimethyl. The reaction is evidenced by the evolution of
16 methane.

17

18 The mole ratio of aluminum in an alumoxane to total metal in the
19 metallocenes which can be usefully employed can be in the range of
20 about 0.5:1 to about 1000:1, and desirably about 1:1 to about 100:1.
21 Preferably, the mole ratio will be in the range of 50:1 to about 5:1 and
22 most preferably 20:1 to 5:1. It is preferred that if an
23 ionic catalyst system, such as that described in
24 EPA 0277004, is employed in the instant invention,
25 that the molar ratio of of first component
26 (cation), to second component (anion) be 1:1 or
27 greater.

28

29 The polyolefin polymers containing terminal unsaturation may be
30 prepared by any suitable process known in the art such as gas, bulk,
31 solution, slurry or high pressure polymerization techniques.
32 Polymerization in solution or in the gas phase is preferred.

33

34 The solvents used in the preparation of the catalyst system are inert
35 hydrocarbons, in particular a hydrocarbon that is inert with respect to

1 the catalyst system. Such solvents are well known and include, for
2 example isobutane, butane, pentane, hexane, heptane, octane,
3 cyclohexane, methylcyclohexane, toluene, xylene and the like.

4
5 Polymerization is generally conducted at temperatures ranging between
6 about 20° and about 300°C, preferably between about 30° and about
7 200°C. Reaction time is not critical and may vary from several hours or
8 more to several minutes or less, depending upon factors such as reaction
9 temperature, the monomers to be copolymerized, and the like. One of
10 ordinary skill in the art may readily obtain the optimum reaction time
11 for a given set of reaction parameters by routine experimentation.

12
13 The catalyst systems described herein are suitable for the
14 polymerization of olefins in solution over a wide range of pressures.
15 Preferably, the polymerization will be completed at a pressure of from
16 about 10 to about 3,000 bar, and generally at a pressure within the range
17 from about 40 bar to about 2,000 bar, and most preferably, the
18 polymerization will be completed at a pressure within the range from
19 about 50 bar to about 1,500 bar.

20
21 After polymerization and, optionally, deactivation of the catalyst (e.g.,
22 by conventional techniques such as contacting the polymerization
23 reaction medium with water or an alcohol, such as methanol, propanol,
24 isopropanol etc., or cooling or flashing the medium to terminate the
25 polymerization reaction), the product polymer can be recovered by
26 processes well known in the art. Any excess reactants may be flashed off
27 from the polymer.

28
29 Techniques known to those skilled in the art for
30 manipulating molecular weight may be employed in
31 the inventive process. If so desired, the polymerization may be
32 carried out in the presence of hydrogen to lower the polymer molecular
33 weight. Care should be taken to assure that terminal ethenylidene
34 unsaturation is not eliminated in the polymer chains. Due to the

1 possibility of hydrogen saturating the terminal groups, it is preferred that
2 the polymers be formed in the substantial absence of added H_2 gas.

3
4 When carrying out the polymerization in a batch-type fashion, the
5 reaction diluent (if any), and the monomer or mixture of monomers are
6 charged at appropriate ratios to a suitable reactor. Care must be taken
7 that all ingredients are dry, with the reactants typically being passed
8 through molecular sieves or other drying means prior to their
9 introduction into the reactor. Subsequently, either the catalyst and then
10 the cocatalyst, or first the cocatalyst and then the catalyst are introduced
11 while agitating the reaction mixture, thereby causing polymerization to
12 commence. Alternatively, the catalyst and cocatalyst may be premixed
13 in a solvent and then charged to the reactor. As polymer is formed,
14 additional monomers may be added to the reactor. Upon completion of
15 the reaction, unreacted monomer and solvent are either flashed or
16 distilled off, if necessary by vacuum, and the low molecular weight
17 polymer withdrawn from the reactor.

18
19 The polymerization may be conducted in a continuous manner by
20 simultaneously feeding the reaction diluent (if employed), monomers,
21 catalyst and cocatalyst to a reactor and withdrawing solvent, unreacted
22 monomer and polymer from the reactor so as to allow a residence time
23 of ingredients long enough for forming polymer of the desired molecular
24 weight and separating the polymer from the reaction mixture.

25
26 The olefin polymers containing terminal unsaturation employed in this
27 invention are further characterized in that up to about 95% and more of
28 the polymer chains may possess terminal ethenylidene-type
29 unsaturation. Thus, one end of such polymers will be of the formula
30 $POLY-C(T^1)=CH_2$ wherein T^1 is C_1 to C_{16} alkyl, preferably C_1 to C_6
31 alkyl, and more preferably C_1 to C_2 alkyl, (e.g., methyl or ethyl) and
32 wherein POLY represents the polymer chain. The chain length of the
33 T^1 alkyl group will vary depending on the comonomer(s) selected for
34 use in the polymerization. A minor amount of the polymer chains can
35 contain terminal ethenyl unsaturation, i.e. $POLY-CH=CH_2$, and a

1 portion of the polymers can contain internal monounsaturations, e.g.
2 POLY-CH=CH(T¹), wherein T¹ is as defined above. Polymers which
3 include a non-conjugated diene component may contain both terminal
4 and internal monounsaturations. Preferably at least about 10 percent,
5 more preferably at least about 50 percent, and most preferably at least
6 about 75 percent (e.g. 75-98%), of such polymer chains exhibit terminal
7 ethenylidene unsaturation. The percentage of polymer chains exhibiting
8 terminal ethenylidene unsaturation may be determined by FTIR
9 spectroscopic analysis, titration, or C¹³NMR or H¹NMR.

10
11 The terminally unsaturated polymers and the composition employed in
12 this invention may be prepared as described in U.S. Patent 4,668,834
13 and in European Patent Publications 128,046, 129,368 and 0260999, the
14 complete disclosures of which are incorporated herein by reference.
15 Other ionic-type activators which may be used to activate the
16 metallocene catalyst component are disclosed in European patent
17 applications 0,277,003 and 0,277,004, the complete disclosures of which
18 are incorporated herein by reference.

19
20 Polymers prepared as described above and having terminal unsaturation
21 useful for the purposes of this invention include polyethylene,
22 polypropylene polybutene as well as copolymers of ethylene with one or
23 more C₃ to C₂₀ alpha monoolefins such as propylene, 1-butene, 1-
24 pentene, 1-hexene, 1-octene, norbornene and the like,

25
26 In the case of
27 ethylene copolymers, the molar ethylene content is preferably in the
28 range of between about 20 and 80 percent, and more preferably
29 between about 30 to about 70 percent. When propylene, butene-1 or
30 other monomers are employed as comonomer(s) with ethylene, the
31 ethylene content of such copolymers is most preferably between about
32 45 and about 65 percent, although higher or lower ethylene contents
33 may be present.

34

1 The olefin polymers containing terminal unsaturation may be of low,
2 medium or high density and may be amorphous or crystalline as a
3 function of the process conditions under which they are produced and
4 the monomer composition. These polymers may have a number
5 average molecular weight (M_n) in the range of about 500 to about
6 50,000, more preferably from about 500 to about 30,000, and most
7 preferably from about 1000 to about 10,000. These olefin polymers
8 generally possess an intrinsic viscosity (as measured in tetralin at 135°C)
9 of between about 0.025 and about 0.9 dl/g., more preferably between
10 about 0.075 and about 0.4 dl/g. The most preferred M_n for these
11 polymers ranges from about 1,000 to about 7,000.

12

13 Compounds which may be alkylated using the above described olefin
14 polymers include phenol or substituted phenols or substituted aromatics
15 of the following general formulas:

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18 a)

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26 b)

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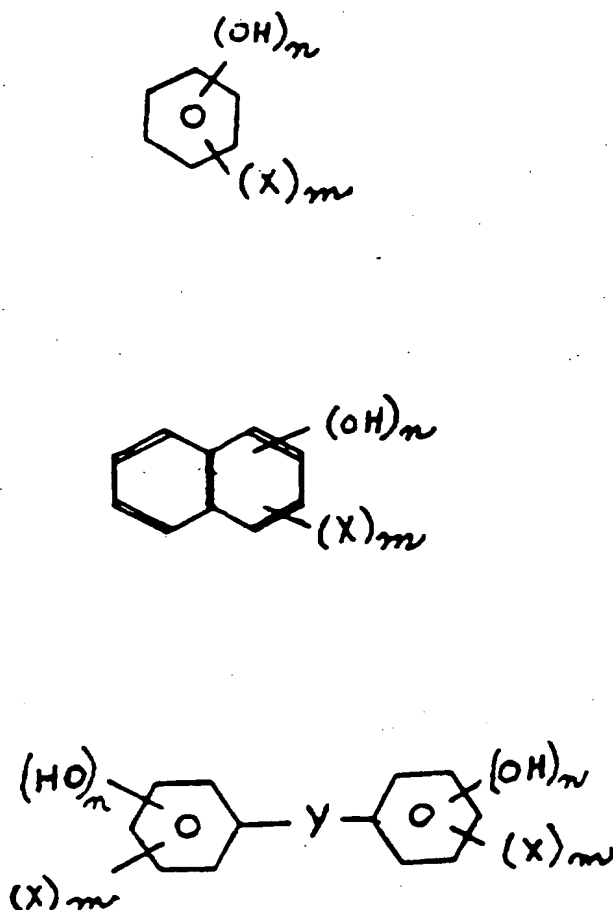
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34 c)

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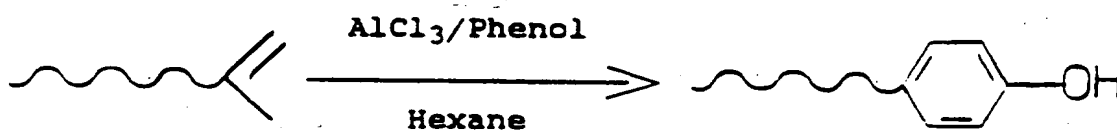
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wherein X is selected from the group consisting of C₁ to C₄ alkyl, and H, Y is selected from the group consisting of a direct link, O, S, S-S, SO, SO₂, Si and C₁ to C₃ alkylidene, n is 0, 1 or 2 and m is 0, 1 or 2, provided that n is at least 1 when m is 0 and X is hydrogen when m is 0.

Examples of suitable phenolic compounds include phenol, 2,6-dimethyl phenol, bisphenol A, 2-methylphenol, 1,5-dihydroxynaphthalene, 1,4-dihydroxy benzene, 4,4'-dihydroxydiphenyl- sulfone and 4-methoxy phenol.

Examples of suitable substituted aromatic compounds include toluene, ethyl benzene, tertiary butyl benzene, anisole as well as alkyl or alkoxy substituted naphthalenes or biphenyls.

The reaction between the terminally unsaturated olefin polymer and the phenolic compound is an electrophilic aromatic substitution reaction which, in the case where an ethylene/propylene copolymer is the olefin polymer and phenol is the phenolic reactant, may be represented by the following equation:



The reaction is conducted in the melt or in solution by contacting the polymer and phenolic reactants with catalytic quantities of an acid catalyst at temperatures of from about 20° to 200°C, more preferably from 20° to about 100°C. Suitable catalysts include BF_3 or BF_3 complexes, sulfuric acid, hydrochloric acid, sulfonic acid, hydrofluoric acid, pyrophosphoric acid, tetraphosphoric acid, arylsulfonic acids and halides of aluminum, titanium, zinc or tin. Preferred acids are Friedel

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1 Crafts or Lewis Acid type catalysts. Solvents which may be employed
2 include aliphatic, cycloaliphatic and aromatic hydrocarbons or
3 halohydrocarbons in which the polymer reactants are soluble such as n-
4 hexane, cyclohexane, monochlorobenzene, dichlorobenzene,
5 trichlorobenzene, toluene, xylene, and the like.

6
7 The phenolic or aromatic reactant and the polymer may be present in
8 the reaction media at the respective ratio of from about 1.0 to about 15
9 moles of reactant per mole of polymer. An excess of about 2:1 to 15:1
10 molar concentration of the phenolic or aromatic reactant is preferred,
11 most preferably an excess of about 3:1 to 7:1.

12
13 As indicated above, this reaction product may be characterized as a
14 polymer product containing the aromatic or phenolic moiety at the
15 terminal position of at least some of the polymer chains. In the case of
16 phenol and 2,6-dimethyl phenol and monosubstituted benzenes,
17 alkylation takes place at the aromatic site para to the hydroxyl or
18 benzene substituent group. This structure is a factor in preventing and
19 minimizing discoloration of the matrix polymer into which the reaction
20 product is incorporated as a stabilizer. Thus, utilization of the
21 terminally unsaturated olefin polymers provides the advantage that well
22 defined polymeric stabilizers containing the phenolic or aromatic moiety
23 positioned only at the terminus of the polymer chain can be produced.

24
25 It is also possible to produce polymeric stabilizers having the phenolic
26 or aromatic moieties positioned randomly along the polymer chain as
27 well as at the terminal position. This may be accomplished by utilizing a
28 random copolymer of at least one olefin and a diene as the starting
29 olefin polymer. In that case, double bonds will be present along the
30 polymer chain and, after alkylation, the phenolic or aromatic moieties
31 will be randomly distributed at positions where some of these double
32 bond sites were present. Where the diene-containing polymer is
33 polymerized using the metallocene catalyst system described above,
34 then a polymer containing both terminal unsaturation and random
35 unsaturation along the polymer chain may be obtained.

1
2 Matrix olefin polymer compositions which can be stabilized by mixing
3 therewith the above-described polymeric stabilizers of this invention
4 include amorphous and crystalline polymers having a number average
5 molecular weight in the range of from about 10,000 up to about
6 2,000,000 and which contain polymerized C₂ to C₂₀ monolefins. These
7 polymers include homopolymers such as ethylene, propylene and
8 isobutylene homopolymers, as well as copolymers of ethylene with one
9 or more alpha olefins having from 3 to 20 carbon atoms. Such materials
10 include high, medium and low density polyethylene, isotactic
11 polypropylene, plastic copolymers of ethylene and
12 propylene, and polybutene.

13 Preferably the stabilizer and
14 matrix polymer are selected such that polymer materials are the most
15 compatible. Most preferably, the polymer component of the stabilizer is
16 of the same species and morphology as the polymer material to which
17 the stabilizer is added.

18
19 The olefin polymer stabilizers of this invention may be blended with the
20 matrix olefin polymer at levels sufficient to impart stability to the
21 polymer matrix, generally in the range of from about 0.05 to about 3%
22 by weight, more preferably from about 0.1 to about 1.5% by weight.
23 The most preferred level of addition is from about 0.1 to about 1.0% by
24 weight.

25
26 The polymeric stabilizers may also be employed in admixture with one
27 or more conventional olefin polymer stabilizers known in the art.
28 Examples include the acid esters such as dilaurylthiodipropionate or
29 distearylthiodipropionate; tetrakis [methylene(3,5-di-tert-butyl-4-
30 hydroxyhydrocin-namate)] methane (IRGANOX 1010); tris (2,4-ditert-
31 butylphenyl)phosphate (IRGATOS 168); tetrakis (2,4-di-tert-
32 butylphenyl-4,4'-biphenylene) diphosphonite (IRGATOS P-EPO); and
33 like materials as well as mixtures thereof.

34

1 The optimum level of stabilizer addition is a function of the molecular
2 weight of the polymeric reactant used to prepare it and the
3 concentration of the phenolic or aromatic groups present in the
4 stabilizer. The higher the molecular weight of the polymer containing
5 terminal unsaturation, the lower the concentration of the phenolic or
6 aromatic groups present in the stabilizer composition, and vice versa.
7 Optimum molecular weight (M_n) of the polymer component of the
8 stabilizer lies within the range of from about 1,000 to about 5,000. The
9 matrix olefin polymer and stabilizer may be blended by any known
10 technique which provides for an intimate admixture of components,
11 such as melt blending. The materials may be dry blended and processed
12 in an extruder or other heat shaping device, or mixtures may be formed
13 in a Banbury or extruder mixer. Melt blending at a temperature above
14 the melting points of the blend components, i.e., above about 200°C, is
15 preferred.

16
17 The following Examples are illustrative of the invention.

18

19

EXAMPLE 1

20

21 In this example, 2,6-dimethyl phenol is alkylated using a terminally
22 unsaturated copolymer of ethylene and 41% by weight propylene
23 produced using the metallocene/alumoxane catalyst system described
24 above. The copolymer had a number average molecular weight (M_n) of
25 3,700, and greater than 75% by weight of the polymer chains contained
26 terminal ethenylidene unsaturation.

27

28 Into a dry 3-necked flask equipped with a condenser, stirrer and
29 nitrogen inlet were added 55.6 gms (0.015m) of the terminally
30 unsaturated ethylene/propylene copolymer and 400 ml of anhydrous
31 cyclohexane to form a solution. To this solution was added 18.3 gms
32 (0.15m) of 2,6-dimethyl phenol and the mixture was stirred for 5
33 minutes. 10.0 gms (0.075m) of aluminum chloride was next added and
34 the mixture was stirred for two hours at ambient conditions under a
35 blanket of nitrogen. The polymeric reaction product was isolated by

1 precipitation using an excess of methanol. The product was stirred with
2 methanol overnight, the methanol was discarded and the product was
3 dried. The product was then purified by dissolving it in hexane and the
4 hexane solution was dried over anhydrous magnesium sulfate. The
5 purified polymer product was then isolated by the evaporation of hexane
6 and it was dried in a vacuum oven at 50°C.

7
8 Analysis of the product using proton NMR spectroscopy showed that the
9 phenolic reactant was quantitatively functionalized with the polymer
10 reactant positioned primarily para to the hydroxyl group.

11 EXAMPLE 2

12
13
14 Example 1 was repeated except that the polymeric reactant used was a
15 terminally unsaturated isotactic polypropylene having a number average
16 molecular weight of about 4,000 and the solvent employed was 1,2,4-
17 trichlorobenzene.

18
19 The reaction product was characterized as a polypropenyl 2,6-dimethyl
20 phenol with alkylation occurring primarily para to the phenolic hydroxyl
21 group.

22 EXAMPLE 3

23
24
25 In this example, toluene is alkylated with a terminally unsaturated
26 copolymer of ethylene and propylene produced using the metallocene
27 catalyst system described above.

28
29 The reactions were carried out in a dry 3-necked flask equipped with a
30 stirrer and a nitrogen inlet. 2.15 gms. (0.001 m) of the terminally
31 unsaturated copolymer of ethylene and propylene having a number
32 average molecular weight of 2,200 (MWD-2.7) was dissolved in 20 ml. of
33 anhydrous toluene at ambient temperature. To this solution was added
34 1.4 gms. (0.01 m) of aluminum chloride and the reaction mixture was
35 stirred for one hour at ambient temperature under a blanket of

1 nitrogen. The end-functionalized EP copolymer was isolated by
2 precipitation in a large quantity of methanol. This polymer was dried in
3 a vacuum oven at 60°C for 36 hours. The proton NMR spectroscopy
4 indicated complete conversion of the terminal double bonds to p-methyl
5 benzene group. The number average molecular weight and the MWD
6 was found to be 3,800 and 2.5 respectively by GPC analysis.

7
8 The stabilizer has utility as a radiation stabilizer for matrix resin systems
9 to which it is added due to the ability of the aromatic moieties to absorb
10 radiation.

11
12 The effectiveness of the polymer reaction products of this invention as
13 heat stabilizers for polyolefin polymers is illustrated in the following
14 Examples. A Ziegler catalyzed polypropylene polymer was used as the
15 matrix polymer.

16 17 18 EXAMPLE 4

19
20 3000 g of isotactic polypropylene granules having a $M(w)$ of 180,364, a
21 $M(n)$ of 55,935 and a polydispersity (M_w/M_n) of 3.2 were combined
22 with 10,800 ppm (about 1.1% by weight) of the stabilizer of Example 1
23 and 500 ppm (0.05% by weight) of calcium stearate which functions as
24 an extrusion processing aid. The mixture was dry blended and kneaded
25 to assure that the additives are uniformly dispersed on the
26 polypropylene granules.

27
28 The polymer composition was extruded on an extruder with a screw
29 diameter of 1 inch. The screw rotated at 52 rpm and the extruder drive
30 was 3.6 to 3.8 amps. A 325 fine screen pack was used to simulate the
31 shear stress encountered in manufacturing. The extrusions were done in
32 an air atmosphere. The temperature of the melt was recorded prior to
33 the die. The average residence time was 30 seconds. The extruded
34 strand was cooled in water and pelletized. The pelletized material was
35 blended and samples collected for melt flow rate determinations.

1
2 The remaining material was then re-extruded. The first extrusion was
3 done at 450°F to simulate production pelletization temperatures. This
4 extruded material sample was labeled "initial". The next five extrusions
5 were at 500°F to simulate typical fabrication and reprocessing
6 temperatures and the samples were labeled 1 through 5 consecutively.
7 Samples were collected after each extrusion for color analysis and melt
8 flow rate determinations.

10 EXAMPLE 5

11
12 Example 4 was repeated exactly as set forth except the quantity of
13 stabilizer employed was reduced to 500 ppm (0.05% by weight). The
14 extrusions were repeated a total of six times as set forth in Example 3.

16 CONTROL

17
18 A control extrusion of polypropylene was performed exactly as set forth
19 in Example 4 except that the stabilizer was eliminated entirely from the
20 formulation. The extrusions were repeated a total of six times as set
21 forth in Example 4.

22
23 Melt flow rate (MFR) was determined for the initial polypropylene and
24 after the initial extrusion and extrusions 1,3 and 5. MFR was measured
25 in g/10 min. of polymer that flows through an orifice under a 2.16 kg.
26 weight at 230°C.

27
28 Yellowness Index (YI) was selected as the best method of measuring the
29 change of color of the pelletized resins. The index was determined
30 under ASTM D-1925. The Yellowness Index of each of the above
31 samples was determined after each extrusion.

32
33 Results of melt flow testing and color testing on samples produced after
34 each extrusion for Examples 4 and 5 as well as the Control are shown in
35 Table 1.

TABLE 1

<u>STATUS</u>	EXTR. TEMP (F)	<u>CONTROL</u>		<u>EX. 4</u>		<u>EX. 5</u>	
		<u>YI</u>	<u>MFR</u>	<u>YI</u>	<u>MFR</u>	<u>YI</u>	<u>MFR</u>
Before Extrusion	----	----	3.0	----	3.0	----	3.0
Initial	450	-4.9	7.4	0.1	6.3	-1.5	10.3
1	500	-4.2	16.5	2.2	8.8	-0.7	16.1
2	500	-4.2	NT	3.4	NT	-0.2	NT
3	500	-3.7	49.6	4.3	14.1	-0.2	30.1
4	500	-3.0	NT	5.0	NT	0.1	NT
5	500	-2.4	99.8	5.5	20.4	0.6	37.3

1 NT: Not tested

2
3 This data shows that the Control sample exhibited considerable polymer
4 degradation after the fifth extrusion as reflected by an increase of MFR
5 from 3.0 to 99.8. GPC data shows that this translates into a molecular
6 weight reduction as shown in Table II.

7
8
9 TABLE II

	<u>Before</u>	<u>After 5th</u>
<u>Polypropylene</u>	<u>Extrusion</u>	<u>Extrusion</u>
Mw	180,364	99,185
Mn	55,935	40,274
Mw/Mn	3.2	2.5

16
17 In contrast, the samples of Examples 4 and 5 exhibited considerably less
18 polymer degradation as reflected by an MFR of only 20.4 and 37.3
19 respectively after the fifth extrusion.

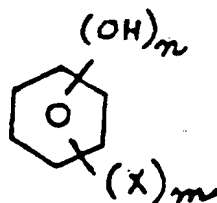
20
21 Yellowness index values for the control show that very little
22 discoloration was encountered over the extrusion cycles as would be
23 expected. Negative values indicate little yellowing whereas positive
24 values indicate a degree of yellowing, the degree of yellowing being
25 reflected by the extent that the value exceeds 0. YI values for Example
26 5 where the polymer composition contains lesser quantities of the
27 stabilizer are quite good. The composition of Example 4 exhibits some
28 yellowing but these values are acceptable and comparable to what is
29 achieved with other commercially available stabilizer systems.

30

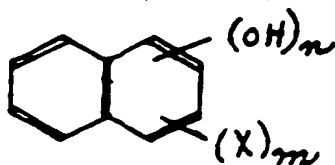
What is claimed is:

1. A heat stabilizer composition comprising the acid catalyzed reaction product of at least one compound having a structure selected from the group consisting of:

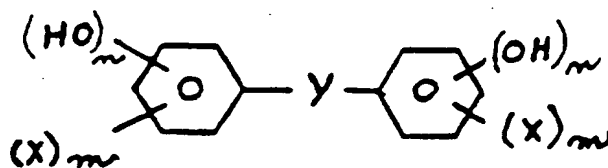
a)



b)



c)



wherein X is selected from the group consisting of H and C₁ to C₄ alkyl, Y is selected from the group consisting of a direct link, O, S, S-S, SO, SO₂, Si and C₁ to C₃ alkylidene; n is 0, 1 or 2 and m is 0, 1 or 2, provided that n is at least 1 when m is 0 and X is hydrogen when m is 0;

and an amorphous or crystalline olefin polymer having an Mn of about 500 to about 50,000 which is a homopolymer or copolymer containing terminal unsaturation, comprising at least one C₂ to C₂₀ monoolefin, said copolymer being essentially free of non-conjugated diene monomer.

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2. The composition of claim 1 wherein said compound and said olefin polymer are present in the reaction media at a respective molar ratio of about 1.0 to about 15.0 moles of said compound per mole of olefin polymer.

3. The composition of claim 1 wherein said molar ratio is about 3.0 to about 7.0 moles of said compound per mole of olefin polymer.

4. The composition of claim 1 wherein said compound is phenolic and is selected from the group consisting of phenol, 2,6-dimethylphenol, bisphenol A, 2-methylphenol, 1,5-dihydroxynaphthalene, 1,4-dihydroxy benzene, 4,4'-dihydroxy-diphenylsulfone and 4-methoxy phenol.

5. The composition of claim 1 wherein said olefin polymer is selected from the group consisting of homopolymers of C_1 to C_4 monoolefins, or a

4 copolymer of ethylene and at least one C₃ to C₂₀
5 monoolefin,
6

1 6. The composition of claim 1
2 wherein said olefin polymer is produced using a
3 metallocene/alumoxane catalyst system.
4

1 7. The composition of claim 6
2 wherein said olefin polymer has a number average
3 molecular weight in the range of from about 1,000 to about
4 10,000
5

1 8. The composition of claim 7
2 wherein said olefin polymer has a number average
3 molecular weight in the range of from about 1,000 to
4 about 7,000.
5

1 9. The composition of claim 1
2 wherein said olefin polymer is a copolymer of ethylene
3 and propylene.
4

1 10. The composition of claim 1
2 wherein said olefin polymer is polypropylene.
3

1 11. A stabilized olefin polymer
2 composition comprising a mixture of:
3

4 a. an olefin matrix polymer; and
5

6 b. stabilizing quantities of the stabilizer
7 composition of claim 1.
8

1 12. The composition of claim 11
2 wherein said matrix polymer is selected from the group
3 consisting of homopolymers of C₂ to C₄ monoolefins and

4 copolymers of ethylene with one or more monoolefins
5 having from 3 to 20 carbon atoms.

6
1 13. The composition of claim 11
2 wherein said matrix polymer is polyethylene.

3
1 14. The composition of claim 11
2 wherein said matrix polymer is polypropylene.

3
1 15. The composition of claim 11 wherein the phenolic compound
2 in the stabilizer composition is selected from the group consisting of phenol,
3 2,6-dimethyl phenol, bisphenol A, 2-methylphenol, 1,5-
4 dihydroxynaphthalene, 1,4-dihydroxy benzene, 4,4'-dihydroxy-
5 diphenylsulfone and 4-methoxy phenol.

6
7
1 16. The composition of claim 15
2 wherein said stabilizer composition is blended with said
3 olefin matrix polymer at a level within the range of about
4 0.05 to about 3% by weight.

5
1 17. A method for enhancing the
2 heat stability of an olefin polymer composition comprising
3 forming a blend of an olefin polymer and heat stabilizing
4 quantities of the stabilizer composition of claim 1.

5
1 18. The method of claim 17 wherein
2 said stabilizer composition is blended with said olefin
3 polymer at a level within the range of about 0.05 to about
4 3% by weight.

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/US93/03119 (22) International Filing Date: 2 April 1993 (02.04.93) (30) Priority data: 07/862,683 3 April 1992 (03.04.92) US (71) Applicant: EXXON CHEMICAL PATENTS INC. [US/ US]; 5200 Bayway Drive, Baytown, TX 77520 (US). (72) Inventors: TERRY, Donna, Jeanes ; 7103 Winding Walk Drive, Houston, TX 77095 (US). GADKARI, Avinash, Chandrakant ; 696 Pineloch Drive, Apt. 1708, Webster, TX 77598 (US).		(74) Agents: BELL, Catherine, L. et al.; Exxon Chemical Com- pany, P.O. Box 2149, Baytown, TX 77522-2149 (US). (81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i> (88) Date of publication of the international search report: 25 November 1993 (25.11.93)
(54) Title: POLYMERIC STABILIZERS FOR POLYOLEFINS (57) Abstract The present invention provides for polymeric stabilizers which are the acid-catalyzed reaction product of a phenolic compound or a ring substituted aromatic compound and an olefin polymer containing either terminal unsaturation and/or pendant unsaturation along the polymer chain. These stabilizers are readily compatible with olefin polymer and copolymer matrixes and offer good protection of the matrix polymer against one or more of heat, oxygen, ultra violet or radiation degradation. Other advantages include low volatilization as well as low tendency to migrate from the polymer matrix.		

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 93/03119

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C08F8/00; C08F8/34; C08F8/42		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C08F	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claims No. ¹³
X	US,A,4 238 628 (P. J. CAHILL) 9 December 1980 see the whole document ---	1-5
X	EP,A,0 418 556 (BAYER AG) 27 March 1991 see column 2, line 17 - column 4, line 9 see column 4, line 24 - line 55; claims 1,2 ---	1-5
A	EP,A,0 295 026 (MITSUI PETROCHEMICALS INDUSTRIES, LTD.) 14 December 1988 see page 6, line 45 - page 7, line 10; example 1 see page 8, line 23 - line 39; claims 1-10 --- -/-	1,6
<p>¹⁰ Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
12 OCTOBER 1993		21. 10. 93
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		PERMENTIER W.A.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
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A	US,A,4 320 021 (R. M. LANGE) 16 March 1982 see claims 1-10 ---	1
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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

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SA 72439

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